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SHORT COMMUNICATIONS

Thermodynamic Simulation of Thermophysical and Elastic Properties of Plutonium

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Abstract—A self-consistent thermodynamic model taking into account phonon anharmonicity effects is used for calculating the temperature dependences of the lattice components of thermophysical and elastic properties of the alpha-phase of plutonium. The theoretical curves are in good agreement with experimental data and make it possible to compare the mechanisms of formation of thermophysical and elastic properties of the alpha- and delta-phases of plutonium. The entropy of both phases is estimated, the role of the lattice magnetic anharmonicity is analyzed, and the key question concerning the reasons for stabilization of the delta-phase of plutonium relative to its α-phase is considered.

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Among six allotropic modifications of plutonium, the alpha (α)- and delta (δ)-phases are of greatest theoretical and practical importance [1]. The calculation of magnetic, thermophysical, and elastic properties of δ-plutonium (for $Pu_{0.96}Ga_{0.04}$ alloy) in [2, 3] showed that the experimentally observed strong temperature dependences of these properties are due to considerable lattice and magnetic anharmonicity (i.e., temperature-dependent spin rigidity). Magnetic anharmonism of $Pu_{1-x}Ga_x$ alloys was also detected in [4], where their anomalous expansion is explained on the basis of the spin-fluctuation model. There are no indications to magnetic anharmonicity of α-Pu because its magnetic susceptibility is almost independent of temperature; however, self-consistent analysis of the reasons for strong temperature dependences of its thermophysical and elastic properties has not been carried out.

When pure α-Pu is doped with a small amount of impurity (as a rule, 2–5% of gallium or aluminum), paramagnetic α-Pu is transformed into almost magnetic δ-Pu; the atomic volumes of the two phases differ by record-high 26%. The physical mechanisms that stabilize the δ-phase relative to the α-phase in the low-temperature region are of fundamental importance and are disputable [5].

In this study, we develop a self-consistent procedure of simulating the thermodynamic properties of α-Pu. The reasons for stabilization of the δ-phase relative to the α-phase are considered on the basis of the results obtained for α-Pu as well as the models for δ-Pu developed in [2, 3].

The basic quantity in the self-consistent thermodynamic model [3] is the characteristic Debye temperature θ, which depends on the temperature and volume; this makes it possible to take into account the effects associated with lattice anharmonicity. It can be proved that the Debye temperature exhibits the following dependence on the elastic moduli:

$$\theta = \frac{\hbar}{k_B}(6\pi^2 N_A^2)^{1/3}\sqrt{\frac{3}{\mu}}\Theta^{1/2}K^{1/2}V^{1/6}, \quad (1)$$

where μ is the molar mass; K is the bulk modulus (BM); V is the molar volume; $\hbar$, k_B, and N_A are the Planck, Boltzmann, and Avogadro constants, respectively; and Θ is an auxiliary function depending on Poisson ratio σ, which characterizes the ratio of shear modulus G to bulk modulus K:

$$\sigma = \frac{1-2G/3K}{2+2G/3K}. \quad (2)$$

The Poisson ratio strongly affects the thermophysical and elastic properties (especially in the low-temperature region); however, its determination involves certain difficulties. Formula (2) and experimental data on elastic moduli can be used only if their values are known in a wide temperature range. In addition, the expression for the shear modulus in terms of the experimentally determined elastic constants is ambiguous in some cases. For this reason, in our earlier study [3], in which the thermophysical and elastic properties of δ plutonium $Pu_{0.95}Ga_{0.05}$ were calculated, we used the method for determining σ based on the attainment of the best agreement between the theoretical and experimental temperature dependences of the mean-square displacement of atoms of the crystal lattice from their

equilibrium positions. However, since experimental data of the standard deviation of α-Pu atoms are not available, we will determine the Poisson ratio using formula (2) and experimental data [6] on elastic moduli.

The molar thermodynamic Gibbs potential in the model considered here is represented by the sum $\Phi = \Phi_0 + \Phi_{ph}$, where $\Phi_0 = \Phi_0(P)$ is the temperature-independent part of the thermodynamic potential (which, however, depends on pressure) and the phonon part of the potential is given by

$$\Phi_{ph} = 3R(3/8\theta + T\phi(z)), \quad (3)$$

where T is the temperature, $z = \theta/T$, and $\varphi(z) = \ln(1 - e^{-z}) - D(z)/3$, $D(z)$ being the standard Debye function. It can be seen from expressions (1) and (3) that the Debye temperature is a function of temperature and appears in the definition of the phonon part of the thermodynamic potential, and this leads to renormalization of the temperature dependences of the lattice components of the entire complex of thermodynamic functions. This renormalization, in turn, also leads to a redefinition of the Debye temperature. Therefore, using a number of experimentally determined parameters (molar mass μ, the values of molar volume V and BCM K at $T = 0$ K, and Poisson ratio σ) as initial data, we can construct, following [3], an iterative procedure for self-consistent calculation of the temperature dependences of the lattice components of various thermal and elastic properties.

The expressions for the lattice contributions to the heat capacity, bulk modulus, and density obtained in the generalized Debye model considered here coincide with those given in [3]. Here, we confine our analysis to the expression derived for the lattice entropy, which will be considered in detail below both of the α-Pu and δ-Pu:

$$S_{ph} = -\frac{d\Phi_{ph}}{dT} = 3R\left\{D(z) - \phi(z) - \left(\frac{3}{8} + \frac{D(z)}{z}\right)\left(\frac{\partial\theta}{\partial T}\right)_F\right\}. \quad (4)$$

To estimate the effect of spin fluctuations on stabilization of the δ-phase, we will also calculate spin-fluctuation entropy S_δ^{el}. Using the expression for the thermodynamic potential of electrons derived in [3] and the thermodynamic definition of entropy in the self-consistent spin-fluctuation theory for the δ-phase, we obtain

$$S_\delta^{el} = -\frac{d\Phi_{el}}{dT} = S_\delta^{s.el} + S_\delta^{pm.el} + \sum_{l=f,d}\left(U^{(l)}\left(k^{(l)}\frac{d(m^l)^2}{dT} + (m^{(l)})^2\frac{d(k^{(l)})}{dT}\right)\right), \quad (5)$$

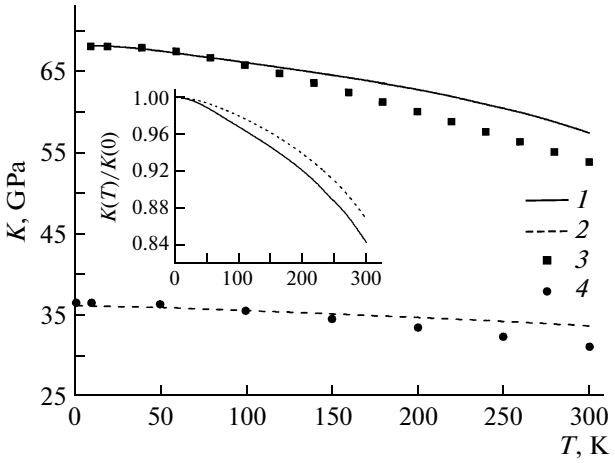

Fig. 1. Temperature dependence of the bulk modulus for plutonium: (here and below) *1*—calculation of the lattice component for the α-phase (this work); *2*—calculation of the lattice component for the δ-phase $Pu_{0.96}Ga_{0.04}$ [3]; squares and circles correspond to experimental results obtained in [6].

where $S_\delta^{s.el}$ is the standard "one-electron" entropy, $S_\delta^{pm.el}$ is the paramagnetic entropy, $m^{(l)}$ is the amplitude of spin fluctuations in the lth band ($l = f, d$), and $k^{(l)}$ is the spin rigidity characterizing the degree of magnetic anharmonicity [3, 4].

The results of calculation of the temperature dependence of the lattice contribution to the BM of α-Pu in comparison with the results obtained in [3] for δ-Pu and with experimental data are shown in Fig. 1. It can be seen that the BM of the α-phase is almost twice as large as the BM of the δ-phase. In addition, α-Pu demonstrates a stronger temperature dependence of the BM ($B(0)/B(300) = 1.28$) as compared to $B(0)/B(300) = 1.23$ for δ-Pu, which indicates noticeable lattice anharmonicity of the α-phase. This fact is confirmed in the inset to Fig. 1, which shows the temperature contributions to the BCM of plutonium in relative units.

Figure 2 shows the results of calculation of the temperature dependence of the lattice contribution to the density of α-Pu as compared to the results obtained in [3] for δ-Pu and experimental data. It can be seen that the theoretical curves for both phases are in good agreement with experimental data. It follows from Fig. 2 that the density of the α-phase is 26% higher than the density of the δ-phase and exhibits a slightly stronger temperature dependence (see the inset to Fig. 2) associated with the effect of lattice anharmonicity.

The data on the lattice heat capacity of the α- and δ-phases of plutonium are compared with experimental results in Fig. 3. The inset to Fig. 3 shows the temperature dependences of the electronic heat capacity of both phases, which were obtained by subtracting the calculated values of the lattice heat capacity from the

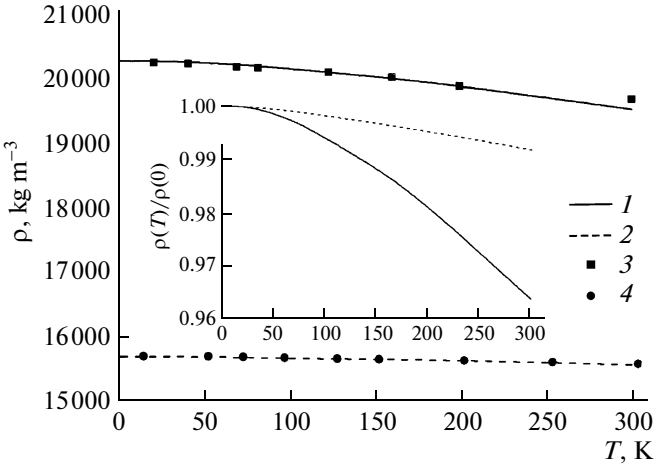

Fig. 2. Temperature dependence of the density of plutonium: squares and circles correspond to experimental results obtained in [8] and [9], respectively.

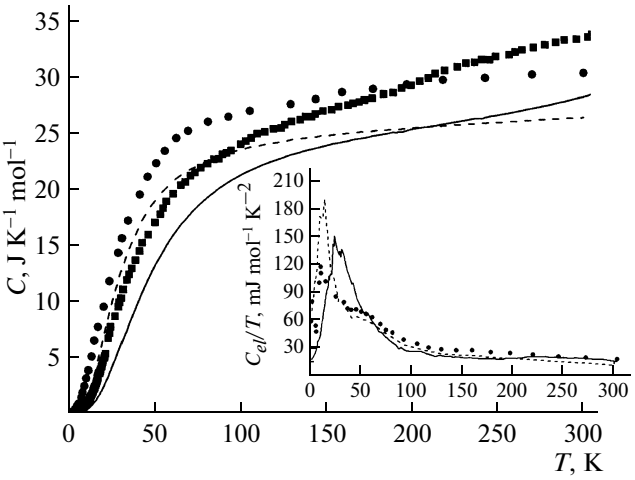

Fig. 3. Temperature dependence of the molar heat capacity for plutonium: squares and circles correspond to experimental results obtained in [1] and [7], respectively; the inset shows the temperature dependence of the electronic heat capacity of plutonium (circles correspond to data from [7]).

experimental data. It can be seen from Fig. 3 that the calculated temperature dependences of both phases considered here are essentially nonlinear and exhibit sharp peaks. The maximum value of the electronic heat capacity of the α-phase is found to be 18 mJ/K^2 (which is in good agreement with the value of γ = 17 mJ/K^2 obtained in [7]); this value is considerably lower than the corresponding value for the δ-phase (γ = 72 mJ/K^2).

Stabilization of the δ-phase of plutonium relative to the α-phase is manifested in its higher entropy. The entropies of both phases at T = 300 K, which are obtained by integrating the experimental data on heat capacity [1], are 6.9 and 8.2 R for the α- and δ-phase, respectively. Thus, the total increment of entropy associated with the α ⟶ δ transformation at T = 300 K is 1.3 R. To determine the physical mechanisms responsible for this transformation, we calculated lattice entropies S_{ph} for both phases at T = 300 K using formula (4): S_{ph} = 5.8 R for the α-phase and S_{ph} = 6.9 R for the δ-phase. The difference ΔS_{ph} between the lattice entropies is 1.1 R, which amounts to 85% of the total entropy increment in the α ⟶ δ transformation. It should be noted that in [1] a lower value of ΔS_{ph} = 0.76 R was obtained.

To determine the physical mechanism for increasing the lattice entropy of the δ-phase, we calculated the anharmonic contributions $S_{ph\text{-}anh}$ to the lattice entropy, which can easily be obtained by subtracting the entropy determined by formula (4) in the harmonic approximation from the total lattice entropy S_{ph}. According to estimates, ratio $S_{ph\text{-}anh}/S_{ph}$ of the anharmonic contribution to the lattice entropy to the "total" lattice entropy is 0.09 for the α-phase and 0.03 for the δ-phase; i.e., lattice anharmonicity makes a larger contribution to the entropy of the α-phase, which also confirms the results of the above comparison of the physical properties. In spite of this, the total lattice entropy is higher for the δ-phase; i.e., the lattice anharmonicity is not responsible for the higher entropy of δ-Pu.

The above analysis of the thermodynamic parameters obtained in this work and in [3] for both phases revealed that the higher entropy of δ-Pu is due to higher values of the Poisson ratio (σ = 0.183 for the α-phase and σ = 0.281 for the δ-phase) and lower values of the bulk modulus (see Fig. 1), which lead to a decrease in the Debye temperature upon the transformation from the α- to the δ-phase. For example, it was found in this work and in [3] that at T = 0 K, θ = 198 K for α-Pu and θ = 124 K for δ-Pu, which in turn leads to an increase in the lattice anisotropy in the δ-phase.

The entropy increment of 0.2 R can be due to other mechanisms (primarily, associated with the electronic subsystem). The calculation of the electronic entropy by formula (5) for δ-plutonium $Pu_{0.96}Ga_{0.04}$ gives a value of 0.6 R (at T = 300 K). If we consider one-electron heat capacity (disregarding magnetic anharmonism), the electron contribution to the entropy is only 0.1 R.

Thus, the increase in the entropy due to the transformation from the α- to δ-phase of plutonium is mainly associated with the increase in the lattice entropy associated with a decrease in the Debye temperature as well as with the emergence of magnetic anharmonicity in the δ-phase.

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